Isotherms of real gases and their comparison with van der Waals isotherms, continuity of states, critical state, relation between critical constants and van der Waals constants, law of corresponding states.

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◷ Ruhul Amin	@February 5, 2023 8:13 PM
# Progress (%)	100

Isotherms of real gases and their comparison with van der Waals isotherms, continuity of states, critical state, relation between critical constants and van der Waals constants, law of corresponding states.

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☰ Difficulty Level	Medium
☰ Mistake type	
☰ Previous Year Questions	

Isotherm: Definition

Isotherms are graphical representations of the relationship between pressure and volume of a gas at a constant temperature. Isotherm means pressure volume curve at constant temperature.

Isotherm for Ideal Gas

- Gases have volume inversely proportional pressure.

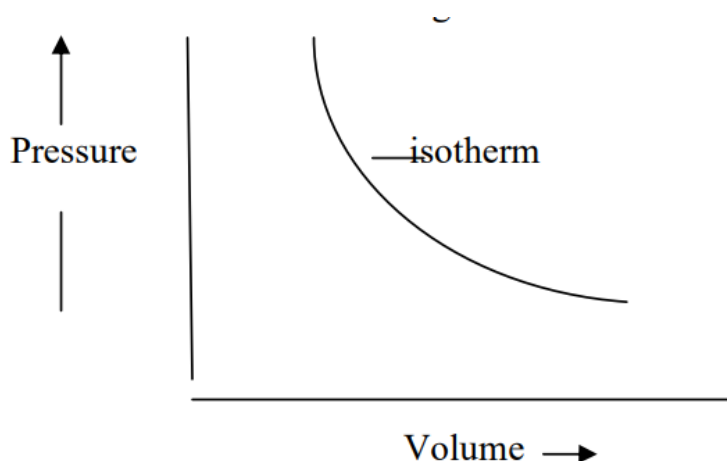- The graph of P vs V in constant temperature is hyperbola.

Fig 2.10 Pressure volume curve at a given temperature

Isotherm for Real Gas

Unlike ideal gases, the behavior of real gases deviates from the ideal gas law due to intermolecular forces and molecular size effects. Isotherms of real gases can show

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characteristics such as compressibility, deviations from Boyle's law, and condensation into a liquid state at high pressures. The shape of an isotherm depends on the properties of the gas, such as its critical temperature and pressure, and the temperature at which the isotherm is taken.

> 💡 We can create 3 cases for real gas isotherms:
>
> 1. PV Isotherm of real gas at temperature Above Critical Temperature
> 2. PV Isotherm of real gas at temperature at Critical Temperature
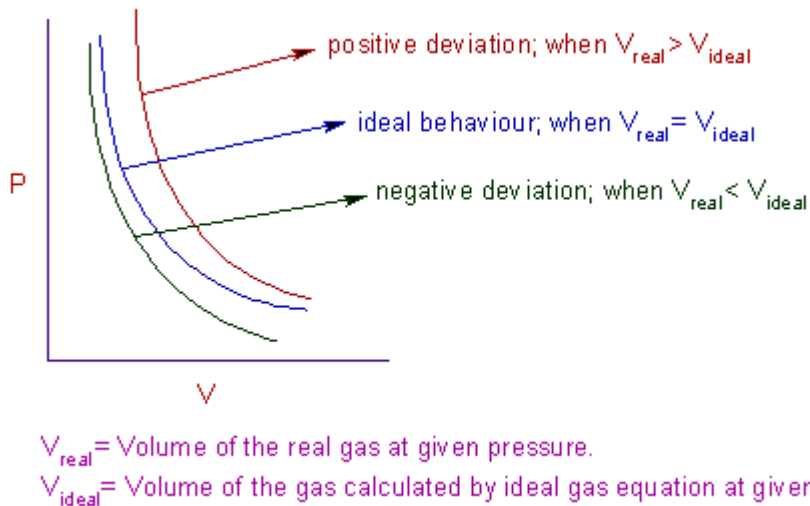> 3. PV Isotherm of real gas at temperature below Critical Temperature

PV Isotherm of real gas at temperature Above Critical Temperature

- Gases have volume inversely proportional pressure.

- As temperature is above critical temperature, gases donot change into liquid state. It just have gaseous state.

- This can be plotted in PV isotherm graph for high temperature as:
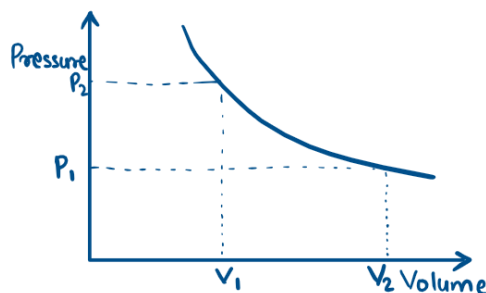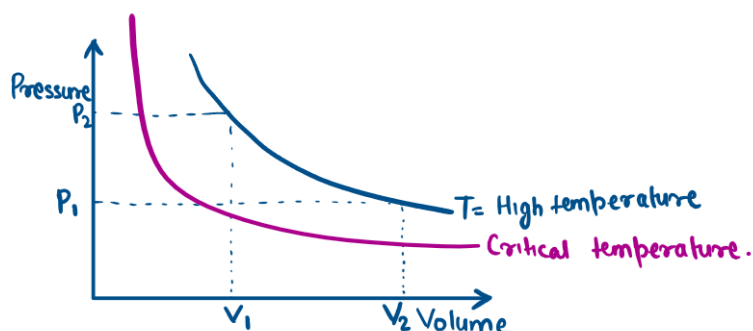

- At temperature above critical temperature , Real gas behaves as ideal gas but donot trace it's exact trajectory. It means that the isotherms obtained by plotting pressure, P against volume, V for real gases do not coincide with that of ideal gas, as shown below.

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positive deviation; when $V_{real} > V_{ideal}$

ideal behaviour; when $V_{real} = V_{ideal}$

negative deviation; when $V_{real} < V_{ideal}$

V_{real} = Volume of the real gas at given pressure.
V_{ideal} = Volume of the gas calculated by ideal gas equation at given pressure.

- It is clear from above graphs that the volume of real gas is more than or less than expected in certain cases. The deviation from ideal gas behaviour can also be expressed by **compressibility factor, Z.**

- The deviation from ideal gas of real gas due to molecular volume and force of attraction in real gases.

PV Isotherm of real gas at Critical Temperature

- Pressure and volume is inversely proportional throught here also.

- At this stage of critical temperature, it is not possible to distinguish between the liquid and gaseous states of the substance as the two forms are existing in equilibrium.

- The PV isotherm at critical temperature is same as the PV isotherm of higher temperature, with just the difference in steepness of the graph. It's graph is more steeper.

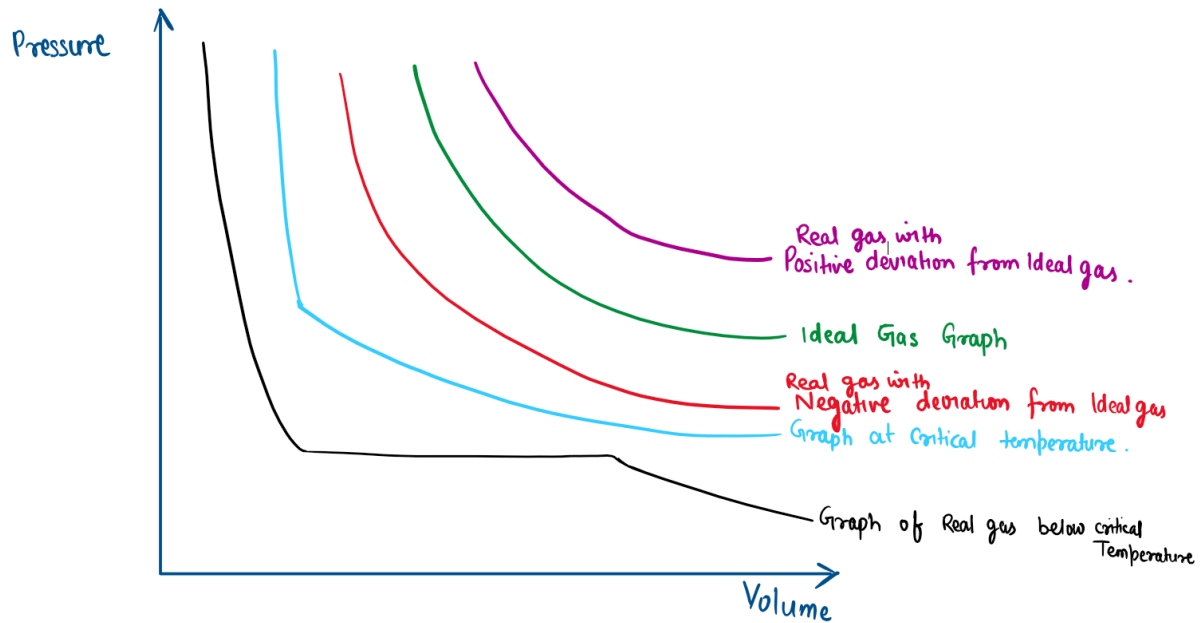- Graphically it can be described as:

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PV isotherm of real gas below critical Temperature

- Below critical temperture, gases change it's phase from gas to liquid.

- During changing of phase from gas to liquid , energy is used up in phase transformation. So, even reducing volume, donot change the pressure.

- The energy are stored as bonds between particles and thus liquid state form from gas.

- When the gas is fully transform into liquid, further energy provided in the system shoots up the pressure .

- The pressure vs volume curve is not inversely proportional throughout. When phase transformation occurs,graph is horizontal , otherwise graph is inversely proportional.

- The graph can be shown as:
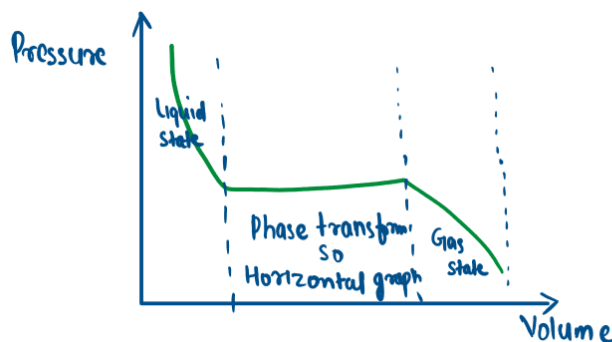
Graph of PV Isotherm of real gas.

All the above three cases graph can be plot in one graph,as:

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The graph shows curves labeled:
- Real gas with Positive deviation from Ideal gas.
- Ideal Gas Graph
- Real gas with Negative deviation from Ideal gas
- Graph at Critical temperature.
- Graph of Real gas below critical Temperature

Axes: Pressure (vertical), Volume (horizontal)

Isotherm of Van der Waals Equation

- **Isotherms** refer to the different curves on the graph, which represent a gas state at different pressure and volume conditions but at constant temperature.
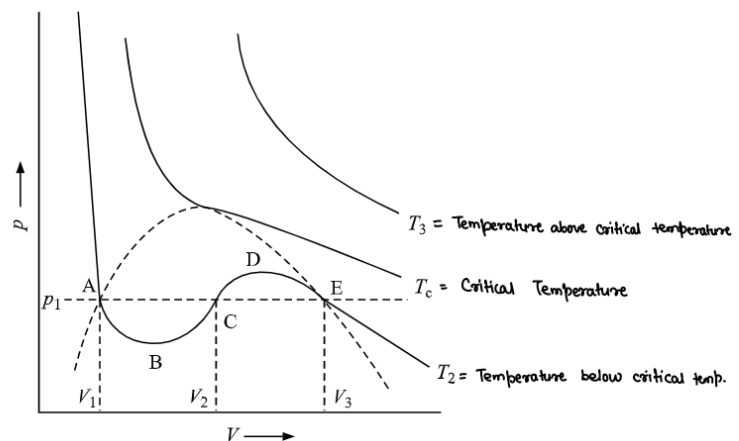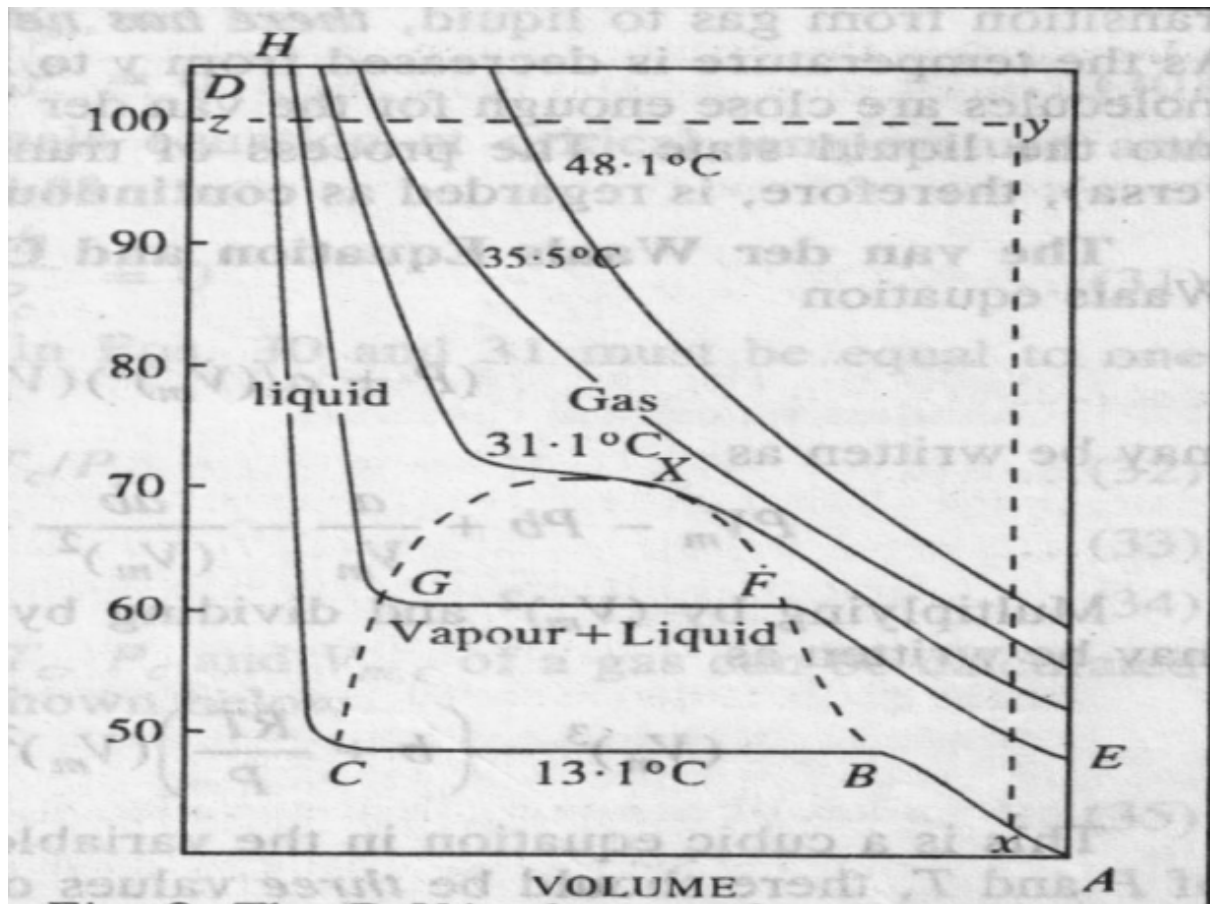
- Isotherm of Van der walls quation can be depicted as :

Labels on graph:
- p (vertical axis), V (horizontal axis)
- T_3 = Temperature above critical temperature
- T_c = Critical Temperature
- T_2 = Temperature below critical temp.
- Points A, B, C, D, E
- p_1
- V_1, V_2, V_3

Fig. _ Van der Waals isotherms

- Main Characteristics of van der waals isotherms are:

- :At higher temperatures such as T3 and in the higher volume region, the isotherms look much like the isotherms for a real gas.

- At a temperature lower than Tc the isotherm exhibits a maximum and a minimum.For certain values of pressure, the equation gives three roots of volume, e.g., V1 , V2 and V3 at pressure p1 .

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- The sections AB and ED of the van der Waals curve at T2 can be realized experimentally. ED represents **supersaturated** (or **supercooled**) vapour and AB represents **superheated** liquid. Both these states are metastable. These are realized only when the volume is changed very slowly. These states are unstable in the sense that slight disturbances are sufficient to cause the system to revert spontaneously into the stable state with the two phases present in equilibrium.

- The section BCD of the van der Waals isotherm cannot be realized experimentally. In this region the slope of the p–V curve is positive. Increasing (decreasing) the volume of such a system would increase (decrease) the pressure. The line BCD also represents the system in the metastable state.

- At the end points of the horizontal line AE, the conversion of gas into liquid or vice versa has just commenced, the system will have the same value of Gibbs function at the points A and E.

Example: Isotherm of Carbon dioxide:

Andrews in 1869 determined the isotherm of carbon dioxide at different temperatures. The isotherms of carbon dioxide determined by him at different temperature are shown in fig 2.11.

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- Consider the first Isotherm at 13.1°C.The point A represents carbon di-oxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve AB. At B liquification of gas commences and there after a rapid decrease in volume takes place at the same pressure as more and more of gas is converted into the liquid state. At C, the gas has been completely liquified. Now, as the liquid is only slightly compressible further increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus along AB, carbon dioxide exists as gas; along BC, it exists partly as gas and partly as liquid while along CD, it exists entirely as liquid.

- The curve EFGH at 21.5°C shows a similar behaviour except that now the liquification commences at higher pressure and the horizontal portion FG, representing decrease in volume, becomes smaller.

- At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces just to a point represented by X. The curve passing through this point X marks the boundary between gaseous carbon dioxide and on the right and liquid carbon dioxide on the left.

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- Andrews noted that above 31.1℃ there was no possibility of liquefaction of carbon dioxide how great the pressure is applied. At this temperature the gas is in **critical state**. The point X is then called the **critical point**. The isotherm passing through this point is called the **critical isotherm** and the temperature corresponding to this isotherm (31.1℃) is called **critical temperature.** The **critical phenomenon** observed by Andrews in connection with carbon dioxide may be observed with any other gas. The pressure required to liquefy the gas at critical temperature is called the **critical pressure** and the volume occupied by one mole of the gas under these conditions is called **critical volume**.

Continuity of State

- Continuity of State is the property of a transition between two states of matter, as between gas and liquid, during which there are no abrupt changes in physical properties.

- There is no difference between the liquid and the gas at the critical temperature.

- Continuity of State was observed by Andrew.

- There is no sharp transition between liquid and gaseous states in contrast to that observed on melting a solid.

- Gases and liquids are just the extreme stages of a fluid, with no fundamental distinction between the two. For this reason, an arbitrary decision has been made for the present discussion to define what is meant by the gaseous state. The definition will be based on the number **density.**

- When gas or liquid (under enough pressure) are heated up above critical temperature, they become gas-like or liquid-like **supercritical fluids,** than can gradually become each other with changing pressure, without phase change or phase boundary. It is like going along the slope instead of making a step.

- There is a unique point for every fluid, called the **critical point.** It is described by a critical temperature, a critical volume, and a critical pressure, at which **liquid and vapour become identical.**
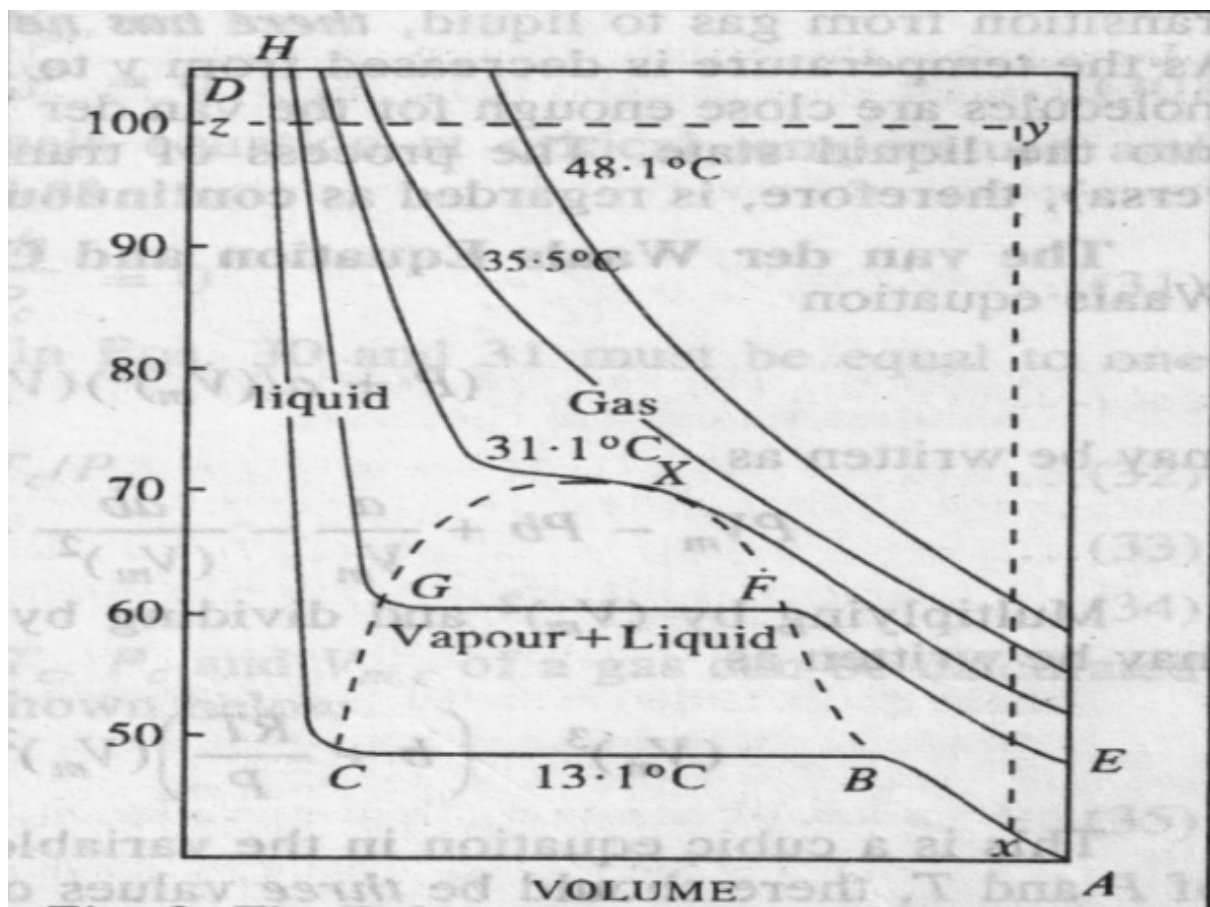
> 🙁 Confuse between Continuity of State and critical points?

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Critical State

The critical state of a substance is a specific set of thermodynamic conditions at which the fluid cannot be distinguished from a gas or a liquid. At the critical state, the liquid and gas phases of a substance have the same density and pressure, and the substance is said to be in a state of supercritical fluid.

Let's understand by PV Isotherm of Carbon dioxide:

- Andrews noted that above 31.1℃ there was no possibility of liquefaction of carbon dioxide how great the pressure is applied. At this temperature the gas is in **critical state**. The point X is then called the **critical point**. The isotherm passing through this point is called the **critical isotherm** and the temperature corresponding to this isotherm (31.1℃) is called **critical temperature.** The **critical phenomenon** observed by Andrews in connection with carbon dioxide may be observed with any other gas. The pressure required to liquefy the gas at

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critical temperature is called the **critical pressure** and the volume occupied by one mole of the gas under these conditions is called **critical volume**.

Definitions of Critical Constants

Critical temperature T_c is the maximum temperature at which a gas can be liquefied, i.e. the temperature above which a liquid cannot exist.

Critical pressure p_c is the minimum pressure required to cause liquefaction at the temperature T_c.

Critical volume V_c is the volume occupied by one mole of a gas at critical temperature T_c and critical pressure p_c.

📌 For every gas, there is a limit of temperature above which it cannot be liquefied, no matter what the pressure is.

Relationship between critical constant and van der waals constants

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RELATION B/W CRITICAL CONSTANT AND VAN DER WAALS CONSTANT

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad , \quad \boxed{V = V_c, \, T = T_c \\ P = P_c}$$

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0$$

$$V = V_c \implies V - V_c = 0 \implies (V - V_c)^3 = 0$$

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$$

$$3V_c = b + \frac{RT_c}{P_c} \, , \quad 3V_c^2 = \frac{a}{P_c} \, , \quad V_c^3 = \frac{ab}{P_c}$$

$$V_c = 3b \, , \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

Step by step derivation:

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Derivation of critical constants from van der Waals constant :

The van der Waals equation for n moles is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \text{.......} (1)$$

For 1 mole

$$\left(P + \frac{a^2}{V^2}\right)(V - b) = RT \quad \text{.......} (2)$$

From the equation we can derive the values of critical canstants P_e, V_e and T_e in terms of a and b, the van der Waals constants, On expanding the above equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \quad \text{......} (3)$$

Multiply equation (3) by V^2/P

$$\frac{V^2}{P}\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$$

$$V^3 + \frac{aV}{P} + - bV^2 - \frac{ab}{V^2} - \frac{RTV^2}{P} \quad \text{......} (4)$$

When the above equation is rearranged in powers of V.

$$V^3 - \left[\frac{RT}{P} + b\right]V^2 + \left[\frac{a}{P}\right]V - \left[\frac{ab}{P}\right] = 0 \quad \text{......} (5)$$

The equation (5) is a cubic equation in V. On solving this equation, we will get three solutions. At the critical point all these three solutions of V are equal to the critical volume V_C. The pressure and temperature becomes P_e and T_e respectively

i.e., $V = V_C$

$V - V_C = 0$

$(V - V_C)^3 = 0$

$$V^3 - 3V_C V^2 + 3V_C{}^2 V - V_C^3 = 0 \quad \text{.......} (6)$$

As equation (5) is identical with equation (6), we can equate the coefficients of V_2, V and constant terms in (5) and (6).

$$-3V_C V^2 = -\left[\frac{RT_C}{P_C} + b\right]V^2$$

$$3V_C = \frac{RT_C}{P_C} + b \quad \text{......} (7)$$

$$3V_C^2 = \frac{a}{P_C} \quad \text{.......} (8)$$

$$3V_C^2 = \frac{ab}{P_C} \quad \text{.......} (9)$$

Divide equation (9) by equation (8)

$$\frac{V_C^3}{3V_C^2} = \frac{ab/P_C}{a/P_C}$$

$$\frac{V_C}{3} = b$$

i.e. $V_C = 3b \quad \text{.......} (10)$

When equation (10) is substituted in (8)

$$3V_C^2 = \frac{a}{P_C}$$

$$P_C = \frac{a}{3V_C^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{3 \times 9b^2} = \frac{a}{27b^2}$$

$$P_C = \frac{a}{27b^2} \quad \text{......} (11)$$

substituting the values of V_C and P_C in equation (7),

$$3VC = b + \frac{RT_C}{P}$$

$$3(3b) = b + \frac{RT_C}{\left(\frac{a}{27b^2}\right)}$$

$$9b - b = \left(\frac{RT_C}{a}\right) = 27b^2$$

$$9b - b = \left(\frac{RT_C}{a}\right) = 27b^2$$

$$8b = \frac{T_C R 27b^2}{a}$$

$$\therefore T_C = \frac{8ab}{27Rb^2} = \frac{8a}{27Rb}$$

$$T_C = \frac{8a}{27Rb} \quad \text{.......} (12)$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3V_C^2 P_C \quad \text{and} \quad b = \frac{V_C}{3}.$$

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The relationship between critical temperature (Tc), Van der Waals constants (a and b), and the gas constant (R):

$$T_c = 8a/27Rb$$

The law of corresponding states
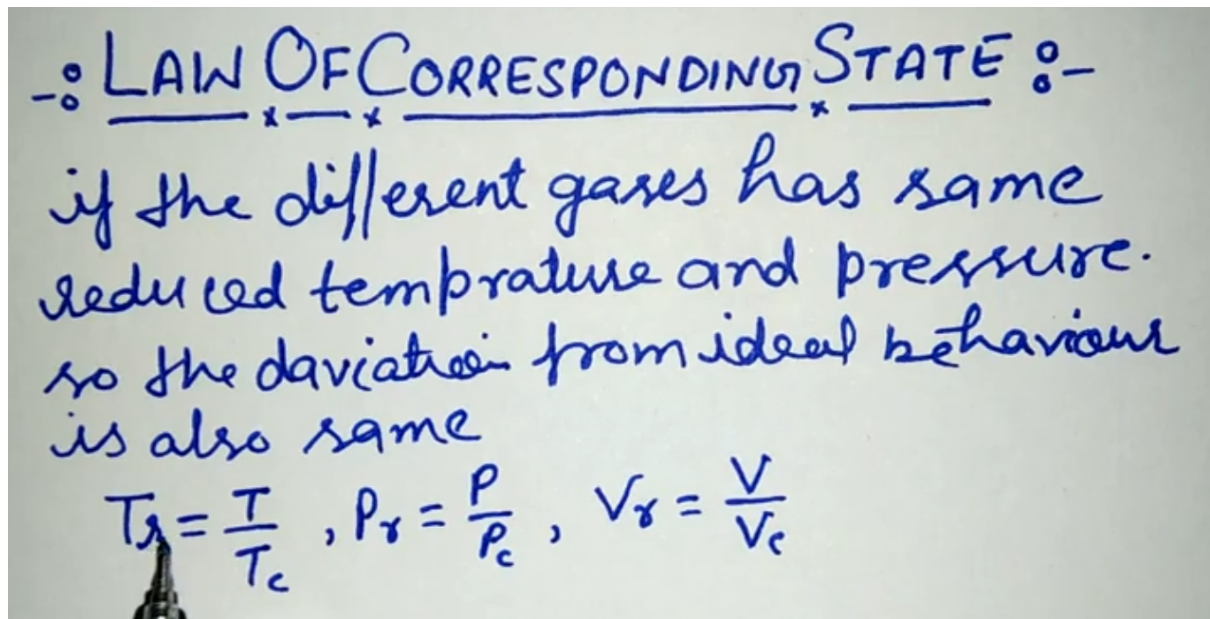
This principle is based on the idea that the interactions between gas molecules are the same, regardless of the type of molecule.

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